

## ***Comparison between Sodium Dodecyl Sulfate and Polyfructose Surfactant Systems in Urea Deproteinisation of Natural Rubber Latex***

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*The use of surfactants in addition to proteolytic enzymes and other protein removing agents such as urea is a common practice in acquiring deproteinised natural rubber latex. In the present work, sodium dodecyl sulphate and a hydrophobically modified polyfructose surfactant were used and compared in urea-deproteinisation of natural rubber latex. The resulting deproteinised NR latex were evaluated for their mechanical stability, protein content, nitrogen content, swelling index, tensile strength and surface morphology. The results showed that the mechanical stability, surface morphology and mechanical properties after aging improved when both sodium dodecyl sulphate and hydrophobically modified polyfructose surfactants were used together. Furthermore, the combination of both surfactants also reduced the extractable protein content, nitrogen content and weight swelling index of the urea deproteinised latex.*

**Key words:** natural rubber; deproteinised NRL; sodium dodecyl sulphate; hydrophobically modified polyfructose surfactant

Natural rubber latex (NRL) has come a long way since it was first discovered by the Mayan people in Mesoamerica<sup>1</sup>. Since its discovery, it has been used extensively and up to the year 2006, the world NRL consumption has increased to 1.2 million tonnes, with Asia taking up 0.98 million tonnes or almost 80% of the total NRL consumption<sup>2</sup>. Due to its superior properties<sup>3</sup>, natural rubber is extensively used in the manufacture of many products such as gloves, balloons, catheters and foams. However, natural rubber has poor

creep and stress relaxation properties due to the non-rubbers<sup>4</sup> associated with the rubber particles.

In order to reduce the non-rubbers, various approaches had been taken, such as multiple centrifugation and deproteinisation<sup>5</sup>. More research on deproteinisation is carried out as compared to the centrifugation process. For instance, deproteinisation of NRL has been performed with various denaturants, such as the mixture of surfactant and proteolytic

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enzyme<sup>6</sup>, combination of surfactant, proteolytic enzyme and salt<sup>7</sup>, and a mixture of urea and surfactant<sup>8</sup>.

In enzymatic deproteinisation, a protease or peptidase enzyme is utilised. The enzyme, obtained from the *Bacillus* bacteria strain<sup>9</sup> is capable of cleaving the amide linkage in the secondary or linear protein structure. In NRL, it is believed that the enzyme cleaves the rubber particle associated proteins in the crosslinked natural rubber chain<sup>10</sup>, therefore removing the proteins from the rubber particles.

In another approach to deproteinise NRL, the latex is treated with urea and surfactant and the synergistic effect of the two materials promotes significant removal of proteins from NRL<sup>11</sup>. In practice, urea promotes the unfolding of proteins and its removal from the lipid monolayer membrane<sup>12</sup> on the surface of the latex particle and is facilitated by the action of surfactant.

Though the surfactant plays an important role in NRL deproteinisation *via* urea route, it is still not confirmed as to what extent the use of surfactant affects the overall properties of NRL. Therefore, in the present investigation, two types of surfactants *i.e.*: an anionic (sodium dodecyl sulphate) and a non-ionic (hydrophobically modified polyfructose) surfactant were used in urea deproteinisation of NRL. The mechanical stability (MST) and

mechanical properties of the resulting dipped films were investigated. The extractable protein content together with the nitrogen content and surface morphology of the films were also studied and compared with high ammonia latex films.

## MATERIALS AND METHODS

### Materials

High ammonia (HA) latex concentrate was purchased from Lee Latex Sdn. Bhd., Malaysia whereas urea and sodium dodecyl sulphate (SDS) were products of System<sup>®</sup> Chemicals, Malaysia. The hydrophobically modified polyfructose or HMP (*INUTEC<sup>®</sup> SPI*) was supplied by BENEIO Bio Based Chemicals, Belgium. The details of the polyfructose surfactant have been described elsewhere<sup>13,14</sup>. Other ingredients used for compounding the latex were supplied by Flexsys and M/S Bayer Ltd. (Mumbai, India).

### Methods

*Deproteinisation.* NRL used was of commercial high ammonia (HA) latex grade. The latex was incubated with urea in the presence of SDS, HMP or combination of both (*Table 1*). The mixtures were stirred overnight and this was followed by centrifugation using

TABLE 1. CONCENTRATION OF SURFACTANTS USED IN THE DEPROTEINISATION PROCEDURE

| Latex              | Surfactant concentration<br>(% per dry rubber content) |
|--------------------|--|
| Control (HA latex) | None   |
| Batch 1            | SDS 0.8%   |
| Batch 2            | SDS 0.8% ; HMP 0.3%                                    |
| Batch 3            | HMP 0.3%   |

a Westfalia centrifugation system. The details of the procedure are described elsewhere<sup>15</sup>.

*Preparation of latex compound.* The dry rubber content of both treated and untreated latexes (Control, Batch 1, 2 and 3) was first measured (*Table 2*) before compounding. Compounding was carried out using the formulation in *Table 3*. The mixture of urea – deproteinised latex and chemicals was placed in a water bath and pre – vulcanised at 60°C for 2 hours. After 2 hours, the resulting compound was taken out of the bath and cooled to room temperature.

TABLE 2. DRY RUBBER CONTENT OF LATEX

| Latex   | Dry Rubber Content (DRC)* |
|---------|---------------------------|
| Control | 59.95                     |
| Batch 1 | 55.25                     |
| Batch 2 | 50.91                     |
| Batch 3 | 56.26                     |

\* Average of two readings

*Preparation of dipped films.* The cooled latex compound was sieved using a muslin cloth to remove any skinning or flocs that may have formed during pre-vulcanisation. In the preparation of dipped films, glass plates were first heated to above 80°C before dipping into 10% calcium nitrate solution. The plates were oven dried at 80°C before dipping into the latex compound for 15 s. Prior to dipping, the total solids content of the latex was reduced to 40% by diluting it with distilled water. The films that formed were air dried for 60 s before being subjected to leaching in water for 120 s. The leached films were then dried in the oven at 85°C for 30 min before vulcanisation at 100°C for 30 min. The vulcanised films were finally subjected to post-leaching in distilled water for 60 s, post-vulcanisation in the oven

at 70°C for 15 min and powdering with corn starch before being stripped from the glass plates.

## Characterisation

*Mechanical Stability Time.* The mechanical stability time of urea-deproteinised latexes was determined using a Klaxon Mechanical Stability Testing Machine at a speed of 14000 r.p.m. with reference to the ISO 35 test method.

*Determination of weight swelling index.* Circular test pieces with diameter of 22 mm were soaked in toluene at room temperature for 48 hours until equilibrium swelling. The swollen samples were weighed and then placed in an oven at 70°C for 24 hours in order to remove the solvent. The weight after drying was measured and the weight swelling index of the films was calculated using the following *Equation 1* where  $W_1$  is the weight of swollen rubber (gram) and  $W_2$  is the weight of deswollen rubber (gram).

$$\text{Weight Swelling Index} = \frac{W_1 - W_2}{W_2} \quad \dots 1$$

*Extractable (EP) Protein Content.* Test specimens with dimension of  $6 \times 6 \text{ cm}^2$  were first extracted using phosphate-buffered saline (PBS) (1 g / 5 mL) at 25°C for 2 hours. The total extractable protein was determined according to the ASTM D5712-99 test method.

*Nitrogen content.* The nitrogen content of the samples was evaluated using the semi – Kjeldahl procedure. Samples were first weighed and digested in a micro Kjeldahl flask before they were steam distilled. The resulting distillate was titrated next with sulphuric acid. The nitrogen content of the films was calculated using the following *Equation 2* where  $V_1$  is the volume of sulphuric acid required for titration

TABLE 3. FORMULATION FOR COMPOUNDING

| Ingredients                 | Amount       |                |
|-----------------------------|--------------|----------------|
|                             | Dry (p.h.r.) | Actual (grams) |
| x % Latex <sup>a</sup>      | 100          | y <sup>b</sup> |
| 20% Potassium laurate       | 0.2          | 1              |
| 10% Potassium hydroxide     | 0.3          | 3              |
| 50% Sulphur                 | 0.7          | 1.4            |
| 50% Perkacit ZDBC           | 0.75         | 1.5            |
| 50% Zinc oxide              | 0.25         | 0.5            |
| 50% Wingstay L <sup>®</sup> | 0.25         | 0.5            |

<sup>a</sup> Dry rubber content (DRC) of latex obtained from the average DRC of batches from *Table 2*;

<sup>b</sup> The actual latex content calculated from the DRC of each batch.

of the contents of the receiving flask (mL);  $V_2$  is the volume of sulphuric acid required for titration of the blank (mL);  $N$  is the normality of sulphuric acid and  $W$  is the weight of the sample (gram).

$$\text{Nitrogen content (\%)} = \frac{(V_1 - V_2)N \times 0.0140}{W} \times 100 \quad \dots 2$$

*Determination of tensile strength.* The tensile strength of the unaged and aged (100°C/22 hours) films was determined using an Instron Tensile Machine 5565 with a crosshead speed of 500 mm/min according to *ISO 37* test method.

*Morphology of latex films.* The films were first cut to about 1 cm × 1 cm and cleaned with acetone to remove dust and stains on the surface of the films. Tweezers were used next to place the films on a glass slide. The surface of the films was then viewed through a Carl Zeiss Axiotech Image Analyzer coupled with a high resolution microscopy camera (AxioCam MRc Rev 3) before capturing the images using the Axiovision Rel 4.6 Software (Carl Zeiss Imaging Systems).

## RESULTS AND DISCUSSION

### Mechanical Stability of Deproteinised NR Latex

In NRL, the proteins that encapsulate the rubber particles provide stability and hence reduce the chances of flocculation or aggregation of rubber particles during transportation or processing. However, during deproteinisation, this layer is removed, therefore increasing the possibility of destabilisation. One important tool used by NRL technologists to measure the stability of NRL is the Mechanical Stability test (MST). During the test, the flocculation of rubber particles is hastened and the mechanical stability time can be estimated.

*Table 4* shows the mechanical stability time of urea deproteinised latexes. It was observed that the MST of latexes from Batch 1 and 2 was higher than the control for both day 1 and day 7. The MST of latex from Batch 3 was however lower than the control on day 1 and reduced further on day 7. It was evident that surfactants affected the MST of the deproteinised latexes with SDS containing

TABLE 4. MECHANICAL STABILITY OF DEPROTEINISED LATEXES

|         | Mechanical stability time (s) |       |
|---------|-------------------------------|-------|
|         | Day 1                         | Day 7 |
| Control | 1420                          | 1320  |
| Batch 1 | >1800                         | >1500 |
| Batch 2 | >1800                         | >1500 |
| Batch 3 | 1200                          | 960   |

latexes giving higher MST than latex with HMP only. SDS, being anionic in nature, not only assists in deproteinisation but also acts as a stabiliser. On the other hand, HMP being a non-ionic surfactant is not expected to contribute to deproteinisation. However, being a polymeric surfactant, HMP has been reported to provide enhanced steric stabilisation<sup>16</sup> due to its structure and conformation. Though so, the stabilisation effect was not observed here as the MST of latex from Batch 3 reduced from 1200 s on day 1 to 960 s on day 7. It is possible that the reduction in MST may be due to the removal of natural stabilisers from the rubber particles. It may also be due to the lower amount of HMP used (0.3%) compared to SDS (0.7%) as the amount of HMP used for this study was referred to a work done previously<sup>14</sup>.

### Weight Swelling Index of Deproteinised NR Latex Films

Figure 1 shows the weight swelling index (WSI) of deproteinised latex films. Swelling index is usually used as an indication of crosslinking density of the films. The higher the WSI, the lower the crosslink density would be. It was observed that the WSI of treated latexes was higher compared to the control (HA latex). Latexes containing HMP showed lower WSI as compared to when SDS alone was used.

The changes in the WSI can be explained using the bonding-adhesive/cement theory. The non-rubbers, in this case the proteins on the outer layer of rubber particles strengthen the interphase between the rubber particles by forming strong cement therefore reducing the effect of the solvent. However, when this cement is removed by deproteinisation for instance, the strength between the interphase is reduced, hence increasing the WSI. The HMP used in this study has been hydrophobically modified by introducing several alkyl groups on the linear polyfructose chain. It is possible that the alkyl groups of the HMP attach themselves onto the rubber particles and behave similarly as the proteins, therefore reducing the WSI of the films.

### Protein Content of Deproteinised NR Latex Films

Figure 2 shows the extractable protein contents of deproteinised NRL films. The latexes were first compounded, dipped, leached and vulcanised prior to testing. The control sample (HA latex) showed the highest extractable protein (EP) content of about 12  $\mu\text{g}/\text{dm}^2$ . Deproteinisation reduced the EP content further to about 50% when SDS or HMI was used. However, a 90% reduction in the EP content was observed when both SDS and HMP were used together (Batch 2).

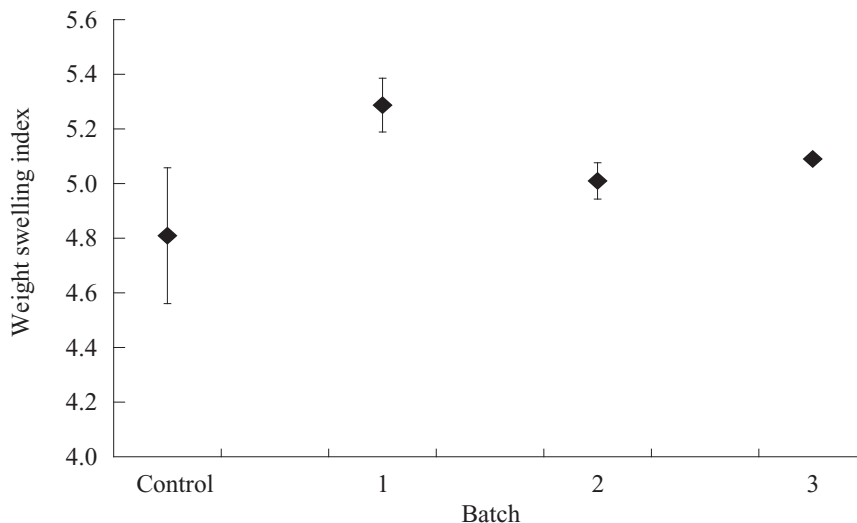


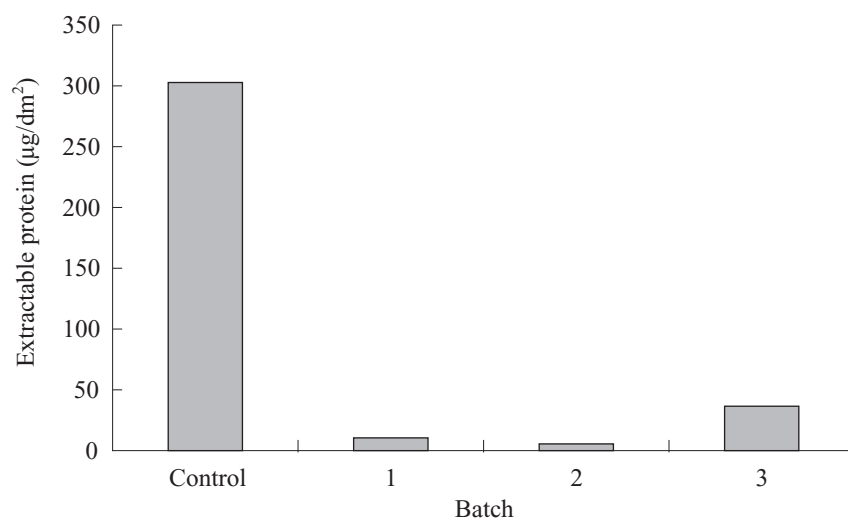
Figure 1. Weight swelling index of deproteinised NR latex films.

Due to the leaching process, most of the extractable proteins in the films might have been removed and this was not shown in the actual results. Therefore, in order to elucidate the effect of surfactant on deproteination, the latexes were cast and the resulting films were retested for EP content. The results obtained are as shown in Figure 3. It was evident that the control gave the highest EP content. The EP content reduced significantly when SDS was used as the surfactant suggesting that SDS assisted in the deproteination. However, the EP content was higher when HMP was used (Batch 3). The combination of surfactants (SDS and HMP) reduced the EP content further, similar to the results shown in Figure 2.

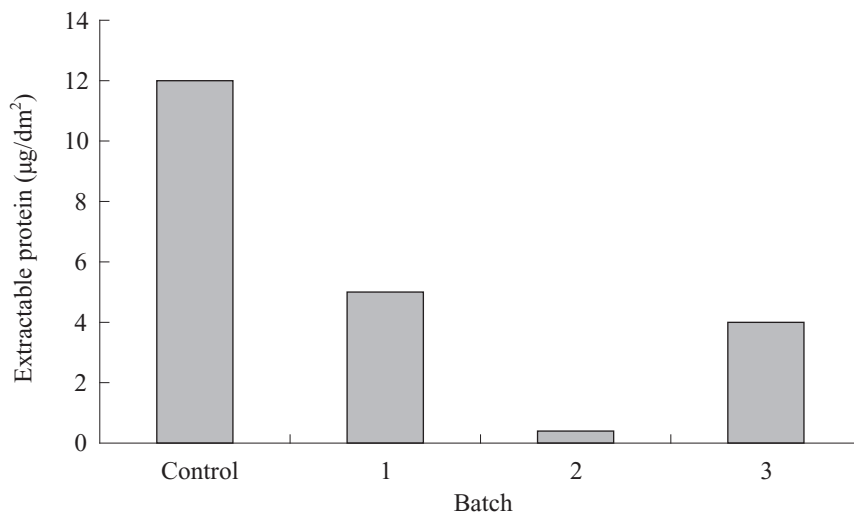
#### Nitrogen Content of Deproteinised NR Latex Films

Deproteination of NRL reduced the protein content, in other words, reduced the nitrogen

containing moieties in the latex. Figure 4 shows the nitrogen content of deproteinised NRL films. It was obvious that the control, which was the untreated latex, contained the highest percentage of nitrogen. The addition of urea together with SDS (Batch 1) reduced the nitrogen content in the films to about 50% compared to the control. Less change was observed when SDS was replaced with HMP (Batch 3) as the difference in nitrogen content of the control and Batch 3 latex films was relatively smaller. However, a marked reduction in the nitrogen content was obtained when HMP and SDS were introduced together into the latex with urea (Batch 2). The nitrogen content was reduced to about 60% compared to the control. It was possible that the reduction in the nitrogen containing moieties be due to some synergistic reaction between SDS and HMP. The presence of HMP at 0.3% may not be sufficient for this matter. However, in order to confirm this, more investigations as to the interaction between these two surfactants are to be conducted.



*Figure 2. Protein content of dipped deproteinised NR latex films.*



*Figure 3. Protein content of cast deproteinised NR latex films.*

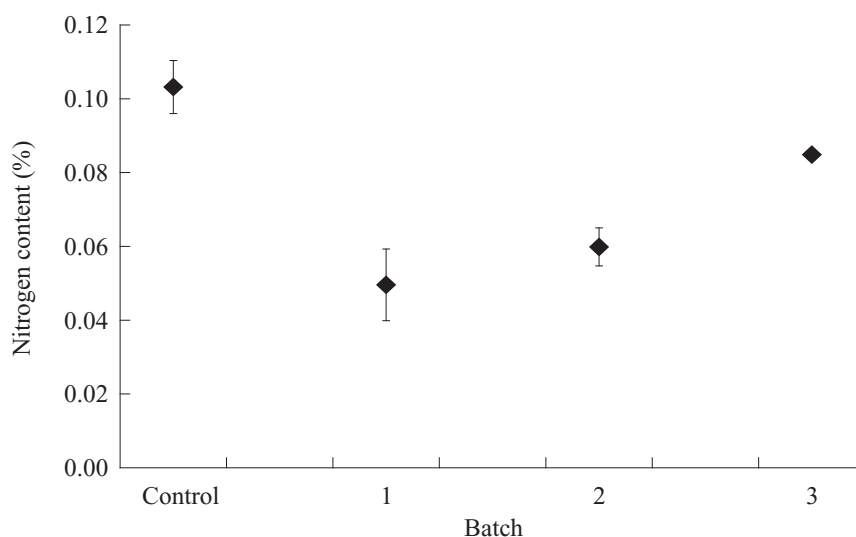


Figure 4. Nitrogen content of deproteinised NR latex films.

TABLE 5. MECHANICAL PROPERTIES OF DEPROTEINISED NR LATEX FILMS\*

| Batch   | M300 (MPa) |      | Tensile Strength (MPa) |             | Elongation at Break (%) |      |
|---------|------------|------|------------------------|-------------|-------------------------|------|
|         | Unaged     | Aged | Unaged                 | Aged        | Unaged                  | Aged |
| Control | 1.12       | 0.79 | 25.0                   | 20.4 (18.4) | 900                     | 950  |
| Batch 1 | 0.92       | 0.58 | 25.6                   | 19.2 (25.0) | 950                     | 1070 |
| Batch 2 | 0.94       | 0.68 | 23.7                   | 21.1 (10.9) | 910                     | 1050 |
| Batch 3 | 0.98       | 0.71 | 26.7                   | 20.0 (25.1) | 650                     | 1050 |

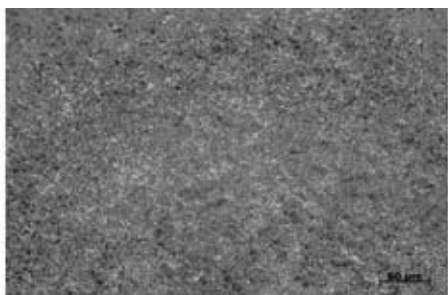
\*Average of three readings. Aging was conducted at 100°C for 22 hours. Values in parentheses indicate the loss of tensile strength in percentage

### Mechanical Properties of Deproteinised NR Latex Films

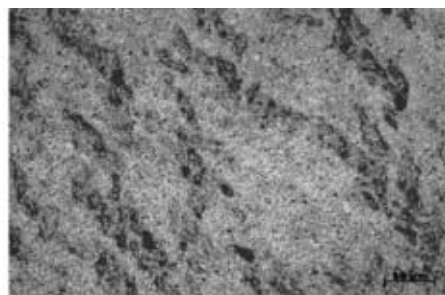
Table 5 shows the mechanical properties of deproteinised NRL films. It is observed that the modulus at 300% elongation (M300) reduced as a result of deproteinisation when compared to the control. The M300 was lower for SDS containing latexes when compared

to HMP containing latexes. However, not much difference was observed in the tensile strength of the films before aging. This is interesting as the tensile strength of the treated films was retained although the proteins were removed through deproteinisation. Aging of the films showed that when SDS and HMP were used individually, the reduction in tensile strength of the films was much higher

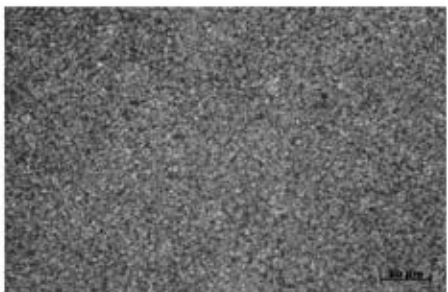




*Control*



*Batch 1*

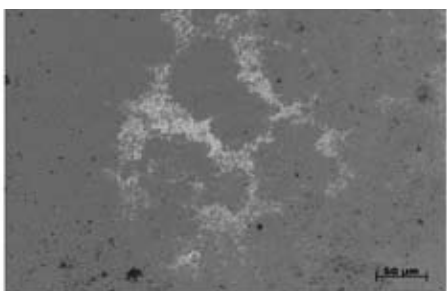


*Batch 2*

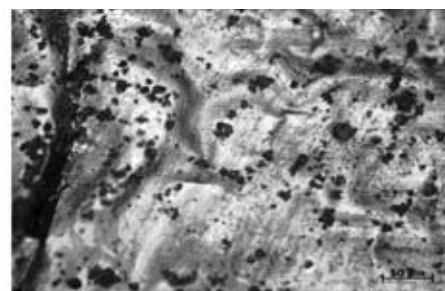


*Batch 3*

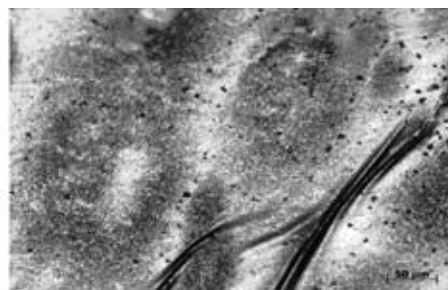
*Figure 5. Surface morphology of dipped deproteinised NR latex films.*



*Control*



*Batch 1*



*Batch 2*



*Batch 3*

*Figure 6. Surface morphology of cast deproteinised NR latex films.*

than the untreated films (control) However, when both SDS and HMP were used in combination, the reduction in tensile strength of the films was much lesser (10.9%) when compared to the control (18.4%). Other values related to tensile measurements such as elongation at break (EB) did not change much for the unaged films when compared to the control except for Batch 3. A marked increase in the EB was observed for the deproteinised films after aging.

### Morphology of Deproteinised NR Latex Films

Figure 5 shows the surface morphology of dipped NRL films. The control, Batch 2 and Batch 3 films showed more even and homogenous surfaces. However, flow marks were observed on the surface of films containing SDS (Batch 1). As dipped films were produced by the coagulation process, the effect of the surfactant was not very evident since the particles were forced to coalesce speedily. Therefore, films were cast so that the latex particles would coalesce naturally (Figure 6). It was observed that SDS affected the latex film formation (Batch 2). Rather than uniform coalescence of rubber particles, two distinct regions representing even and uneven surfaces (light and dark) were dispersed throughout the film. The addition of HMP with SDS improved the film surface further (Batch 2). No clusters of regions of rubber particles as observed for films from Batch 1 were observed in films from Batch 3 which contained only HMP.

### CONCLUSION

In the present study, sodium dodecyl sulphate (SDS) and a hydrophobically modified polyfructose (HMP) were used in the urea deproteinisation of NRL. The results showed

that the combination of both surfactants improved the properties of urea deproteinised latex compared to when the surfactants were used individually. The combination of both SDS and HMP increased the mechanical stability time of the latex and reduced the extractable protein content, nitrogen content and weight swelling index of the latex. Improvements in the mechanical properties of the latex were observed after aging although no significant changes were observed before aging. The surface morphology of urea deproteinised latex also improved when both SDS and HMP were used together.

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